

## TITLE OF THE INVENTION

### MATERIAL FOR COPPER ELECTROPLATING, METHOD FOR MANUFACTURING SAME AND COPPER ELECTROPLATING METHOD

## BACKGROUND OF THE INVENTION

This invention relates to a material for copper electroplating (hereinafter also referred to as "copper electroplating material"), a method for manufacturing a copper electroplating material and a copper plating method, and more particularly to a copper electroplating material which is fed as a copper ion supply to a copper plating bath in which an object to be plated is subjected to copper electroplating, a method for producing such a copper electroplating material, and a copper plating method using such a copper electroplating material.

One of techniques of subjecting an object to be plated (hereinafter also referred to as "plated object") to copper plating which have been conventionally known in the art is an copper electroplating method wherein a material for copper plating or a copper plating material is introduced into a sulfuric acid solution acting as an electrolyte and a current is flowed between an insoluble anode and a plated object acting as a cathode. In the method, copper oxide prepared by subjecting basic copper carbonate to thermal composition is used as the copper plating material (see Japanese Patent No. 2,753,855).

Copper oxide is widely used as a material for ferrite. Also, it is used as a copper ion supply for a bath for electroless plating of copper as disclosed in Japanese Patent Application Laid-Open Publication No. 80116/1991. Copper oxide is generally produced by subjecting a mill scale of copper, cuprous oxide or copper hydroxide to a heat treatment. However, a copper mill scale is hard to dissolve in an electrolyte, to thereby fail to be used as a material for copper plating. Also, cuprous oxide contains a chlorine ion ( $\text{Cl}^-$  (hereinafter merely referred to as " $\text{Cl}^-$ ")) in a large amount, leading to a failure in copper plating. Further, the Japanese publication described above (Japanese Patent Application Laid-Open Publication No. 800116/1991) discloses that copper oxide may be obtained by heating copper hydroxide to a temperature within a range of between  $60^\circ\text{C}$  and  $100^\circ\text{C}$ . However, use of cupric hydroxide for copper electroplating causes a failure in plating of copper because it contains a chlorine ion and sulfur (S) derived from  $\text{SO}_4^{2-}$  (hereinafter merely referred to as " $\text{SO}_4^{2-}$ ") in a large amount. On the contrary, copper oxide obtained by subjecting basic copper carbonate to thermal decomposition may be used as a material for copper plating, because a content of Cl and S (derived from  $\text{SO}_4^{2-}$ ) therein is reduced. However, use of copper oxide obtained by thermal decomposition of basic copper carbonate as a copper plating material causes problems.

More particularly, the copper oxide is usually used as a material for

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ferrite, so that it is required that copper oxide is reduced in weight reduction in a calcination step in manufacturing of ferrite. For this purpose, a heating temperature employed in thermal decomposition of copper oxide or a heat treatment thereof is generally as high as 900°C or more. Unfortunately, although the thus-obtained copper oxide is readily dissolved in an electrolyte as compared with usual copper oxide, it fails to exhibit satisfactory solubility. This causes a period of time in which the copper oxide fed to a copper plating bath is dissolved in an electrolyte to be increased and renders a concentration of copper ions in the electrolyte nonuniform, leading to scattering in quality of an article which has been plated (hereinafter also referred to as "plated article") and a deterioration in throughput capacity.

Also, a furnace for thermal decomposition of the copper oxide is generally constituted by a rotary kiln of the type heated directly by a flame in view of thermal efficiency. However, it causes the copper oxide to be partially formed into cuprous oxide and metallic copper due to contact of the copper oxide with the flame which is a reducing flame. The thus-formed cuprous oxide and metallic copper lead to an increase in an insoluble residue which is an impurity when it is dissolved in a sulfuric acid solution which is an electrolyte. It is required to keep a concentration of copper in the electrolyte constant. However, this renders a concentration of copper in the electrolyte nonuniform, resulting in quality of an article plated being deteriorated.

Further, impurities which are introduced in a small amount into the basic copper carbonate from a material for the basic copper carbonate, such as alkaline metals (Na and K), alkaline earth metals (Mg and Ca), a chlorine ion, S derived from  $\text{SO}_4$  and the like are increased in concentration by, for example, about 1.4 to 1.5 times in the copper oxide obtained by thermal decomposition. Accumulation of a chlorine ion in the plating bath renders an article plated coarse or causes formation of nodular or needle-like deposits on the article, resulting in the article being defective. Also, accumulation of S derived from  $\text{SO}_4$  therein not only adversely affects the plating, but renders control of a  $\text{SO}_4$  concentration in the plating bath difficult, leading to scattering in quality of an article plated. Further, accumulation of alkaline metal and/or alkaline earth metal in the plating bath causes likelihood that sulfates thereof are deposited on an article plated, leading to an increase in frequency at which the plating bath must be renewed or refreshed.

Thus, continuous running of copper plating while directly using the copper oxide as a material therefor causes the above-described impurities to be accumulated in the plating bath. Accumulation of the impurities to an upper limit determined from a viewpoint of control of the plating causes a failure in copper plating, so that it is required to renew or refresh the plating bath earlier than expected. Unfortunately, such renewal or

refreshment of the plating bath causes a disadvantageous increase in plating cost, leading to an increase in cost of an article plated.

Also, it is known in the art that basic copper carbonate is used as a copper plating material in the copper electroplating described above, as disclosed in Japanese Patent No. 2,753,855, of which the disclosure is incorporated herein by reference. Basic copper carbonate is suitable for use as a material for copper plating from a viewpoint of the fact that it is increased in solubility. Also, basic copper carbonate is produced by reacting an aqueous cupric chloride solution or an aqueous cupric sulfate solution with an aqueous solution containing a carbonate ion. Use of an aqueous cupric chloride solution causes the basic copper carbonate to contain a chlorine ion and that of an aqueous cupric sulfate solution causes it to contain  $\text{SO}_4$ , however, a content of such impurities in the basic copper carbonate is relatively reduced. In a plating plant, in view of the fact that accumulation of a Cl ion and S derived from  $\text{SO}_4$  in the plating bath leads to a deterioration in copper plating, it is carried out to monitor a concentration of such impurities in the plating bath, to thereby renew or refresh the plating bath when the impurities accumulate to an upper limit determined from a viewpoint of control of the plating. However, such renewal or refreshment of the plating bath causes a significant increase in plating cost, leading to an increase in cost of the article plated. Therefore, it would be highly desirable to minimize a content of the impurities in the basic copper carbonate.

#### SUMMARY OF THE INVENTION

The present invention has been made in view of the foregoing disadvantage of the prior art.

Accordingly, it is an object of the present invention to provide a material for copper electroplating or a copper electroplating material which is capable of being highly easily dissolved in an electrolyte, to thereby minimize formation of an insoluble residue in a plating bath.

It is another object of the present invention to provide a copper electroplating material which is capable of being reduced in impurities.

It is a further object of the present invention to provide a copper plating method which is capable of being suitably applied to the copper electroplating material described above.

In accordance with one aspect of the present invention, a method for manufacturing a material for copper electroplating or a copper electroplating material adapted to be fed as a copper ion supply to a copper plating bath in copper electroplating is provided. The method includes the step of heating basic copper carbonate to a temperature of  $250^\circ\text{C}$  to  $800^\circ\text{C}$  in an atmosphere which is not rendered reducing or reductive to carry out thermal decomposition of the basic copper carbonate, to thereby produce

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easily soluble copper oxide constituting the copper electroplating material. The term "heating of the basic copper carbonate in the atmosphere which is not rendered reducing or reductive" referred to herein is intended to mean heating by means of an electric furnace rather than direct heating by means of, for example, a burner.

In the present invention, basic copper carbonate which is a material for easily soluble copper oxide may be commercially available. Alternatively, it may be obtained by mixing an aqueous solution of copper chloride, copper sulfate or copper nitrate with an aqueous carbonate solution of, for example, alkaline metal, alkaline earth metal or ammonia( $\text{NH}_4$ ) and then reacting the aqueous solutions with each other while heating them. In this instance, mixing between the aqueous carbonate solution and the aqueous solution of copper chloride, copper sulfate or copper nitrate may be carried out by charging the carbonate in the form of a solid into the aqueous solution of copper chloride, copper sulfate or copper nitrate to dissolve the former in the latter or charging copper chloride, copper sulfate or copper nitrate in the form of a solid into the aqueous carbonate solution to dissolve the former in the latter. The copper electroplating material of the present invention is soluble or easily dissolved in an electrolyte, to thereby be suitable for use as a copper plating material fed to the electrolyte in which an insoluble anode and a plated object acting as a cathode are arranged. In this instance, when the copper plating material contains such impurities as described above in a large amount, an article plated is deteriorated in quality. Thus, when the basic copper carbonate contains impurities such as alkaline metal (Na, or K), alkaline earth metal (Mg, or Ca) and/or an anion ( $\text{Cl}^-$ , or  $\text{SO}_4^{2-}$ ) or the like in a large amount, the easily soluble copper oxide is preferably washed with water.

In accordance with another aspect of the present invention, a copper plating method is provided. The copper plating method includes the steps of feeding the copper electroplating material described above to an electrolyte in which an insoluble anode and a plated object acting as a cathode are arranged and subjecting the plated object to copper plating.

In accordance with a further aspect of the present invention, a method for manufacturing a copper electroplating material fed as a copper ion supply to a copper plating bath in copper electroplating is provided. The method includes the steps of mixing an aqueous cupric chloride solution and an aqueous solution containing a carbonate ion with each other to prepare a mixed solution, keeping the mixed solution at a pH within a range of between 8.0 and 9.0 and a temperature within a range of between  $75^\circ\text{C}$  and  $90^\circ\text{C}$  to form basic copper carbonate, and subjecting the basic copper carbonate to solid-liquid separation and washing, so that the basic copper carbonate may have a chlorine concentration of 80ppm or less.

In accordance with this aspect of the present invention, a method for manufacturing a copper electroplating material fed as a copper ion supply to a copper plating bath in copper electroplating is provided. The method includes the steps of mixing an aqueous cupric sulfate solution and an aqueous solution containing a carbonate ion with each other to prepare a mixed solution, keeping the mixed solution at a pH within a range of between 8.0 and 9.0 and a temperature within a range of between 75°C and 90°C to form basic copper carbonate, and subjecting the basic copper carbonate to solid-liquid separation and washing, so that the basic copper carbonate may have a SO<sub>4</sub> concentration of 200ppm or less.

In the present invention, mixing between the aqueous cupric chloride solution or aqueous cupric sulfate solution and the aqueous carbonate ion-containing solution is carried out while controlling a pH of the mixed solution. In this regard, the inventors found that the mixing at a temperature of 95°C or more causes a substantial difference between the apparent pH and the actual pH, thus, feed of the aqueous solutions based on pH control causes the basic copper carbonate to contain a large amount of impurities.

In view of the above, in accordance with this aspect of the present invention, a method for manufacturing a copper electroplating material fed as a copper ion supply to a copper plating bath in copper electroplating is provided. The method includes the steps of feeding an aqueous cupric chloride solution and an aqueous solution containing a carbonate ion to a reaction tank while adjusting a feed ratio between both aqueous solutions so that a molar ratio of a copper ion to a carbonate ion in a mixed solution of both aqueous solutions may be within a range of between 1:1.3 to 2.6, keeping a temperature of the mixed solution at a level of 95°C or more without pH control of the mixed solution to produce basic copper carbonate, and subjecting the basic copper carbonate to solid-liquid separation and washing, to thereby provide the copper electroplating material constituted by the basic copper carbonate.

When the cupric sulfate is substituted for the cupric chloride, the feed rate is so adjusted that a molar ratio between the copper ion and the carbonate ion is 1:2.3 to 4.6.

Mixing between the aqueous cupric chloride or cupric sulfate solution and the aqueous carbonate ion-containing solution may be also carried out by charging cupric chloride or cupric sulfate in the form of a solid into the aqueous carbonate solution, charging the carbonate in the form of a solid into the aqueous cupric chloride or cupric sulfate solution, or introducing carbon dioxide into the aqueous cupric chloride or cupric sulfate solution.

In accordance with still another aspect of the present invention, a method for manufacturing basic copper carbonate fed as a copper ion supply

to a copper plating bath in copper electroplating is provided. The method includes the steps of feeding an aqueous cupric sulfate solution and an aqueous solution containing a carbonate ion to a reaction tank while adjusting a feed ratio between both aqueous solutions so that a molar ratio of a copper ion to carbonate ion in a mixed solution of both aqueous solutions may be within a range of between 1:2.3 to 4.6, keeping a temperature of the mixed solution at a level of 95°C or more without pH control of the mixed solution to produce basic copper carbonate, and subjecting the basic copper carbonate to solid-liquid separation and washing, to thereby provide the copper electroplating material constituted by the basic copper carbonate.

### BRIEF DESCRIPTION OF THE DRAWINGS

These and other objects and many of the attendant advantages of the present invention will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings; wherein:

Fig. 1 is a flow diagram showing an embodiment of a method for manufacturing a material for copper electroplating or a copper electroplating material according to the present invention;

Fig. 2 is a schematic block diagram showing a plating apparatus used in copper electroplating of the present invention by way of example;

Fig. 3 is a graphical representation showing a variation in conductivity shown in Table 1 with time;

Fig. 4 is a graphical representation showing a variation in conductivity shown in Table 1 with time;

Fig. 5 is a flow diagram showing another embodiment of a method for manufacturing a copper electroplating material according to the present invention; and

Fig. 6 is a flow diagram showing a further embodiment of a method for manufacturing a copper electroplating material according to the present invention.

### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Now, the present invention will be described with reference to the accompanying drawings.

First, described is a method for manufacturing a material for copper electroplating or a copper electroplating material which is constituted of significantly soluble copper oxide.

In the present invention, basic copper carbonate which is a material for significantly soluble copper oxide may be commercially available. Alternatively, it may be obtained by mixing an aqueous solution of copper

chloride, copper sulfate or copper nitrate with an aqueous carbonate solution of, for example, alkaline metal, alkaline earth metal or ammonia(NH<sub>4</sub>), reacting both aqueous solutions with each other while heating them, depositing a reaction product, and then separating the reaction product by filtration. In this instance, mixing between the aqueous carbonate solution and the aqueous solution of copper chloride, copper sulfate or copper nitrate may be carried out by charging the carbonate in the form of a solid into the aqueous solution of copper chloride, copper sulfate or copper nitrate to dissolve the former in the latter or charging copper chloride, copper sulfate or copper nitrate in the form of a solid into the aqueous carbonate solution to dissolve the former in the latter.

In the illustrated embodiment, basic copper carbonate prepared as described above is used.

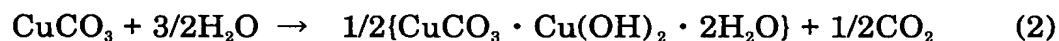
Referring first to Fig. 1, an embodiment of a method for manufacturing a material for copper electroplating or a copper electroplating material which is basic copper carbonate is illustrated in the form of a flow diagram. For example, an aqueous solution of cupric chloride (CuCl<sub>2</sub>) which has a copper concentration of 10% by weight and an aqueous solution of alkaline metal carbonate such as, for example, an aqueous sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) solution having a carbonate concentration of 7% by weight are charged in a reaction tank 1 so that a mixed solution of both aqueous solutions has a pH of 7.0 to 9.0. Then, the solutions thus mixed are stirred for, for example, 30 minutes using a stirring means 11 while being heated so that the mixed solution has a temperature of, for example, 70°C. Such heating of the mixed solution may be carried out by providing any suitable bubbling means constituted by an air diffusing pipe (not shown) or the like the reaction tank 1 and introducing bubbled steam into the mixed solution using the bubbling means.

Now, the reaction noted above will be described.

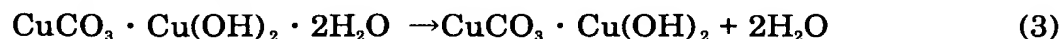
First, copper carbonate is produced according to the following reaction formula (1):



Then, the thus-formed copper carbonate is hydrated as indicated by the following chemical formula (2), to thereby provide basic copper carbonate dihydrate:



Then, water is removed from the basic copper carbonate dihydrate to provide anhydrous basic copper carbonate as indicated by the following chemical formula (3):



The basic copper carbonate thus formed is then deposited or precipitated in

the form of a powder. Then, a valve 2 is rendered open to draw out the thus-precipitated slurry therethrough to a centrifugal separator 2, in which the slurry is subjected to centrifuging to separate a solid matter of the slurry from a mother liquor thereof. Then, the solid matter is placed in a drier 3, to thereby be dried therein, resulting in basic copper carbonate being obtained in the form of a powder.

Copper ion sources for the basic copper carbonate may include aqueous solutions of copper chloride, as well as copper salts such as, for example, copper sulfate, copper nitrate and the like. Carbonate ion sources may include carbonates of alkaline metals such as sodium carbonate, sodium bicarbonate, potassium carbonate and the like, as well as carbonates of alkaline earth metals such as calcium carbonate, magnesium carbonate and barium carbonate, ammonium carbonate  $((\text{NH}_4)_2\text{CO}_3)$ , and the like.

Then, the above-described basic copper carbonate which is in the form of a powder is introduced into a heating furnace such as, for example, a rotary kiln 4, in which it is heated to a temperature between, for example, 250°C and 800°C for thermal decomposition thereof. In the illustrated embodiment, the heating furnace may be constituted by a rotary kiln which is so constructed that a rotary pipe 41 made of, for example, stainless steel and adapted to revolve about an axis thereof is arranged in a manner to be slightly inclined and a heater 42 is arranged so as to surround the rotary pipe 41, resulting in the basic copper carbonate powder being carried by rotation of the rotary pipe 41, as shown in Fig. 1. Heating of the basic copper carbonate in such a manner prevents an atmosphere in which the carbonate powder is heated from being reducing or reductive. In the illustrated embodiment, the basic copper carbonate is not heated directly in a burner. This is for the reason that such direct heating of copper carbonate leads to formation of a reducing atmosphere, which causes reduction or deoxidation of a part of copper carbonate and/or copper oxide formed by decomposition of copper carbonate, to produce cuprous oxide ( $\text{Cu}_2\text{O}$ ) and/or metallic copper ( $\text{Cu}$ ).

Metallic copper is insoluble or hard to dissolve in an aqueous sulfuric acid solution used as an electrolyte when copper oxide is used as a material for copper plating or a copper plating material, to thereby form an insoluble residue, resulting in a new filter being required for removing the residue. Also, formation of metallic copper and cuprous oxide renders feed of copper to a plating bath nonuniform, resulting in quality of an article plated being considerably scattered. Thus, it is essential to prevent the heating atmosphere in which the basic copper carbonate is heated from being rendered reducing or reductive.

Setting of the heating temperature at 250°C permits copper oxide to be formed by heating the basic copper carbonate for, for example, about 2



hours. However, heating at a temperature as low as 200°C fails in thermal decomposition of the basic copper carbonate. Also, a differential thermal analysis reveals that a temperature at 200°C likewise fails in thermal decomposition of the basic copper carbonate. Thus, it is required that the heating is carried out at a temperature of 250°C or more. Also, in order to reduce a period of time required for the thermal decomposition to increase production efficiency, the heating is preferably carried out at a temperature of 350°C or more. However, the heating at a temperature above 800°C causes copper oxide formed to be reduced in solubility. Thus, the heating is required to take place at a temperature of 800 °C or less. In order to obtain copper oxide which is more highly easily dissolved in the electrolyte, the heating temperature is preferably 600°C or below.

In this instance, the above-described impurities are contained in a large amount in the material for copper plating or copper plating material, an article plated is deteriorated in quality. Thus, when the basic copper carbonate contains a large amount of impurities such alkaline metals (Na, and K), alkaline earth metals (Mg, and Ca), anions (a chlorine ion  $\text{Cl}^-$ , and a sulfate ion  $\text{SO}_4^{2-}$ ), and the like, the highly soluble copper oxide obtained by thermal decomposition is preferably washed with water.

Thus, in the illustrated embodiment as well, after formation of the copper oxide, it is charged in a washing tank 5 which is filled therein with pure water acting as wash liquid and washed while stirring the wash liquid using a stirring means 51. Then, a valve 52 is opened to draw a mixed slurry of water and copper oxide out of the washing tank 5, resulting in the slurry being fed to a centrifugal separator 6 or a filter, in which the slurry is dewatered. Subsequently, the dewatered slurry is dried in a drier 7, so that copper oxide may be obtained in the form of a powder. Pure water such as distilled water, ion-exchanged water or the like may be used as the wash liquid. Alternatively, water further reduced in impurity such as superpure water may be used for this purpose.

Now, an apparatus for practicing copper plating in which copper oxide is used as a supply for a copper plating material will be described with reference to Fig. 2 by way of example. In Fig. 2, reference numeral 8 designates a plating bath, which is filled therein with plating liquid including sulfuric acid acting as an electrolyte and copper oxide dissolved therein. The plating liquid has an insoluble anode 81 and a cathode 82 immersed therein. The insoluble anode 81 is constituted, for example, by a titanium plate having platinum or platinum-iridium coated thereon at a ratio of 7:3 and connected to a positive electrode of a DC power supply E. The cathode 82 which is constituted by an object to be plated or a plated object and may be in the form of, for example, a metal plate is connected to a negative electrode of the DC power supply E. Reference numeral 83 designates a dissolution tank for dissolving copper oxide therein. The

dissolution tank 83 is fed with a predetermined amount of copper oxide in the form of a powder from a hopper 84 acting as a copper oxide feed source. Then, the copper oxide is dissolved in an aqueous sulfuric acid solution in the dissolving tank 83 while being stirred with a stirring means 85. The copper oxide thus dissolved is fed to the plating bath 8 by means of pumps P1 and P2 for the next copper plating, when the amount of copper ion in the plating bath 8 is reduced. Reference character F is a filter.

In the illustrated embodiment, as described above, copper oxide is prepared by subjecting basic copper carbonate to thermal decomposition at a temperature within a range of between 250°C and 800°C. This permits the copper oxide to be easily dissolved in an aqueous sulfuric acid solution as described hereinafter. Also, the thermal decomposition does not take place in a reducing atmosphere, to thereby minimize or substantially prevent production of an insoluble residue such as cuprous oxide, metallic copper and the like. This almost prevents application of load to the filter and renders a copper ion concentration in the copper plating bath stabilized, when copper oxide is used as a material for copper plating or a copper plating material.

Basic copper carbonate inherently contains an anion and a cation depending on a material therefor. For example, when basic copper carbonate is made of an aqueous solution of cupric chloride ( $\text{CuCl}_2$ ) and an aqueous solution of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), it contains a chlorine ion and a sodium ion. Also, when cupric sulfate ( $\text{CuSO}_4$ ) is substituted for cupric chloride, basic copper carbonate prepared contains a sodium ion and S derived from a  $\text{SO}_4$  ion. Washing of the basic copper carbonate fails to permit the impurities such as a chlorine ion, S of a  $\text{SO}_4$  ion, a sodium ion, a potassium ion and the like to be substantially removed therefrom, leading to a failure in purification of the carbonate. However, as will be noted from examples described below, when the basic copper carbonate is subjected to thermal decomposition to obtain copper oxide, followed by washing of the copper oxide, the impurities may be reduced. Thus, use of copper oxide as a material for copper plating or a copper plating material permits a period of time in which a concentration of the impurities reaches an upper limit determined from a viewpoint of control of the plating bath to be increased, to thereby reduce the number of times of renewal or refreshment of the plating bath, leading to a reduction in plating cost.

The illustrated embodiment of the present invention will be understood more readily with reference to the following examples; however, these examples are intended to illustrate the invention and not to be construed to limit the scope of the invention.

#### Example 1-1

Copper oxide was obtained by subjecting basic copper carbonate to thermal decomposition at a temperature of 400°C for about 60 minutes

according to the embodiment described above.

#### Example 1-2

Copper oxide was obtained by subjecting basic copper carbonate to thermal decomposition at a temperature of 600°C for about 60 minutes according to the embodiment described above.

#### Example 1-3

Copper oxide was obtained by subjecting basic copper carbonate to thermal decomposition at a temperature of 700°C for about 60 minutes according to the embodiment described above.

#### Example 1-4

Copper oxide was obtained by subjecting basic copper carbonate to thermal decomposition at a temperature of 750°C for about 60 minutes according to the embodiment described above.

#### Example 1-5

Copper oxide was obtained by subjecting basic copper carbonate to thermal decomposition at a temperature of 800°C for about 60 minutes according to the embodiment described above.

#### Comparative Example 1

Copper oxide was obtained by subjecting basic copper carbonate to thermal decomposition at a temperature of 900°C for about 60 minutes according to the embodiment described above.

In order to grasp solubility of copper oxide fed as a material for copper plating or a copper plating material to the copper plating bath, a powder of copper oxide obtained in each of Examples 1-1 to 1-5 and Comparative Example 1 was charged in an amount of 550g into 10 l of an aqueous sulfuric acid solution having a  $\text{H}_2\text{SO}_4$  concentration of 245 g/l and dissolved therein, to thereby obtain each of sample solutions. Then, conductivity of each of sample solutions thus obtained was measured in the course of dissolution of copper oxide in the aqueous sulfuric acid solution. Results of the measurement were as shown in Table 1.

Table 1

Elapsed Time (sec)	Conductivity (S/m) of Copper Oxide					
	900°C	800°C	750°C	700°C	600°C	400°C
0	68.7	70.9	70.8	70.2	70.9	73.4
5	65.2	55.1	49.0	48.8	44.9	55.1
10	56.4	49.2	46.2	46.0	42.2	47.8

15	53.6	46.4	44.8	45.2	41.2	45.4
20	51.9	45.2	44.6	44.3	41.0	45.2
25	50.4	44.6	44.2	44.0	40.7	45.0
30	49.2	44.1	44.0	43.5	40.7	45.0
35	48.2	44.0	43.4	43.5	40.7	45.0
40	47.4	43.8	43.4	43.5	40.7	45.0
45	46.8	43.7	43.4	43.5	40.8	45.0
50	46.1	43.5	43.4	43.5	40.9	45.0
55	45.6	43.5	43.4	43.4	40.9	45.1
60	45.3	43.5	43.5	43.4	40.9	45.2
65	44.9	43.5	43.4	43.4	41.0	45.2
70	44.4	43.5	43.5	43.5	41.1	45.2
75	44.2	43.5	43.5	43.5	41.1	45.2
80	44.0	43.4	43.6	43.6	41.0	45.2
85	43.8	43.5	43.6	43.6	41.2	45.2
90	43.5	43.5	43.5	43.5	41.2	45.1
95	43.5	43.6	43.5	43.5	41.1	45.2
100	43.4	43.6	43.6	43.6	41.2	45.2
105	43.2	43.5	43.5	43.6	41.2	45.2
110	43.0	43.6	43.5	43.5	41.2	45.2
115	43.0	43.6	43.6	43.6	41.2	45.2
120	43.0	43.7	43.6	43.6	41.2	45.2

Also, a variation in the thus-obtained conductivity with time is shown in Figs. 3 and 4. Further, supposing that time at which the conductivity is rendered constant is defined as a dissolution termination point and a period of time between charging of the copper oxide powder and the dissolution point termination is defined as dissolution time, the dissolution time was measured in each example. Results of the measurement were as shown in Table 2.

Table 2

	Example					Comparative
	1-1	1-2	1-3	1-4	1-5	Example 1
TD Temp* (°C)	400	600	700	750	800	900

Dissolution Time	25	25	30	35	50	110
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#### TD Temp\*: Thermal Decomposition Temperature

As will be noted from the thus-obtained results, a temperature of thermal decomposition of the basic copper carbonate up to 800°C ensures that the copper oxide is easily dissolved in the aqueous sulfuric acid solution, however, an increase in the temperature to a level of 900°C causes the copper oxide to fail to be easily dissolved therein. Also, a reduction in thermal decomposition temperature from 800°C to 600°C permits a reduction in dissolution time or permits the copper oxide to be easily dissolved in the solution. Thus, it will be noted that the thermal decomposition temperature is preferably below 800°C, and, for example, more preferably 600°C or below. A reduction in solubility of the copper oxide due to an increase in temperature would be due to the reason that an increase in temperature promotes solid phase sintering of the copper oxide obtained by thermal decomposition.

#### Example 2

Copper oxide was obtained by subjecting basic copper carbonate to thermal decomposition at a temperature of 400°C for about 60 minutes according to the embodiment described above.

#### Comparative Example 2-1

The procedure described in Example 2 was substantially repeated except that a rotary kiln which has a reducing atmosphere formed therein due to direct heating by a burner was used.

#### Comparative Example 2-2

The procedure described in Example 2 was substantially repeated except that a temperature at which the basic copper carbonate is thermally decomposed was set to be 900°C.

A powder of copper oxide obtained in each of Example 2, and Comparative Examples 2-1 and 2-2 was charged in an amount of 550g into 10 l of an aqueous sulfuric acid solution having a  $H_2SO_4$  concentration of 245 g/l and dissolved therein, to thereby obtain each of sample solutions. Then, the sample solutions each were subjected to filtration by means of a filter paper and then the amount of an insoluble residue left on the filter paper was measured. Results thereof were as shown in Table 3.

Table 3

	Example 2	Comparative Example 2-1	Comparative Example 2-2
Amount of Residue (mg)	22	1100	280
Ratio of Residue * (%)	0.01 or less (0.004)	0.20	0.05

Ratio of Residue\*: amount of residue/amount of copper oxide charged(mg) x 100

The results of Table 3 reveal that thermal decomposition of the basic copper carbonate in a reducing atmosphere causes an increase in the amount of the insoluble residue. Also, it will be noted that the thermal decomposition at a temperature as high as 900°C still shows the increased amount of insoluble residue formed by thermal decomposition even in a non-reducing atmosphere although it is considerably reduced as compared with that formed in a reducing atmosphere. On the contrary, the present invention highly reduces the amount of insoluble residue formed.

#### Example 3

Copper oxide was obtained by subjecting basic copper carbonate to thermal decomposition at a temperature of 400°C for about 60 minutes according to the embodiment described above. Then, the copper oxide was washed with water under conditions described below. Then, concentration of Na and Cl contained in copper oxide before the washing and those thereafter were measured by inductively coupled plasma-analysis of emission spectrum (ICP-AES) or titration. Results of the measurement were as shown in Table 4.

Table 4

	Copper Oxide	
	Before Water Washing	After Water Washing
Na Concentration (ppm)	1440	84
Cl Concentration (ppm)	58	10

Washing Conditions: 500g of the copper oxide powder was charged in 4500g of water, stirred for 10 minutes, and filtered followed by water washing. The water washing was carried out using 5000g of water with respect to 500g of copper oxide powder.

The results indicate that although water washing of basic copper carbonate fails to reduce a concentration of Na and Cl, that of copper oxide is highly effective to reduce a concentration of impurities.

#### Example 4

Copper electroplating was executed under the following conditions while using copper oxide having a chlorine concentration(Cl concentration) of about 20 ppm as a copper supply.

Electroplating Conditions:

Anode: Titanium plate coated with platinum alloy  
(Pt:Ir=7:3)

Cathode: Copper plate

Electrode area: 10cm x 10cm

Current density, current, voltage: 1 A/dm<sup>2</sup>, 1A, 2.2V

Copper concentration: 18 g/l in terms of Cu

Concentration of sulfuric acid: 180 g/l in terms of H<sub>2</sub>SO<sub>4</sub>

A chlorine concentration in the plating bath at the time of starting of the copper plating was adjusted to be about 20ppm. When copper oxide was fed so as to keep the copper concentration in the plating bath constant, a chlorine concentration in the plating bath was not increased but reduced. Thus, in order to keep the chlorine concentration in the plating bath constant, chlorine was added at a rate of 5 to 20 ppm/day thereto. As a result, it would be considered that the amount of chlorine generated from the anode is increased as compared with the amount of chlorine contained in copper oxide fed. The cathode ultimately obtained had a highly flat and smooth surface.

#### Comparative Example 4

Copper electroplating was executed under substantially the same conditions as in Example 4 described above while using copper oxide having a chlorine concentration of about 140 ppm as a copper supply.

A chlorine concentration in the plating bath at the time of starting of the copper plating was adjusted to be about 20ppm. When copper oxide was fed so as to keep the copper concentration in the plating bath constant, a chlorine concentration in the plating bath was increased at a rate of 2 to 4 ppm/day. This would be due to the fact that the amount of chlorine contained in the copper oxide fed was increased as compared with the amount of chlorine generated from the anode. After 40 days, a chlorine concentration in the plating bath was increased to a level of about 150ppm. The cathode ultimately obtained had a rough surface as compared with that obtained in Example 4 described above.

Now, an embodiment of a method for manufacturing a material for copper electroplating or a copper electroplating material consisting a basic copper carbonate according to the present invention will be described with

reference to Fig. 5, which generally shows an apparatus of the batch type for executing such a method. In a method of the illustrated embodiment, an aqueous cupric chloride( $\text{CuCl}_2$ ) solution having a copper concentration, for example, of 10% by weight and an aqueous solution containing a carbonate ion are fed through feed lines 100 and 200 to a reaction tank 9 in which, for example, pure water is previously filled so that a mixed solution of both aqueous solutions has a predetermined pH value within a range of between 8.0 and 9.0. For example, aqueous solution containing a carbonate ion may be an aqueous solution of sodium carbonate having a carbonate concentration of 7% by weight. Then, the mixed solution is stirred for a predetermined period of time by stirring means 91, to thereby lead to a reaction between cupric chloride and sodium carbonate.

In Fig. 5, reference numeral 301 designates a pH detection section for detecting a pH (hydrogen ion concentration) of the solution in the reaction tank 9. Reference numeral 302 is a temperature detection section for detecting a temperature of the solution in the reaction tank 9. Detection signals detected by the pH detection section 301 and temperature detection section 302 are fed to a control section 400. The feed lines 100 and 200 are provided with flow control sections 101 and 201, respectively. The flow control sections 101 and 201 each may be constituted by a valve. The flow control sections 101 and 201 each are operated to control a feed rate of each of the aqueous cupric chloride solution and aqueous sodium carbonate solution so that a pH detected by the pH detection section 301 may have a predetermined value.

Then, heated water vapor (steam) is introduced into the mixed solution in the reaction tank 9 while being bubbled through a bubbling means 303 such as an air diffusing pipe or the like arranged in the reaction tank 9, to thereby heat the mixed solution so as to permit it to have a predetermined temperature within a range of between  $75^\circ\text{C}$  and  $90^\circ\text{C}$ , resulting in a reaction of the mixed solution being carried out. The reaction may take place for, for example, two hours. The above-described heating of the mixed solution may be controlled by adjusting the degree of opening of a valve 305 provided on a steam line 304 through the control section 400 depending on a signal detected by the temperature detection section 302.

The above-described reaction is advanced according to the chemical formulas (1) to (3) described above, so that basic copper carbonate may be formed in reaction tank 9 and precipitated in the form of a powder therein. Then, a valve 92 is opened, so that a slurry which is the precipitated powder may be drawn out to a centrifugal separator 500, in which a solid matter of the slurry is separated from a mother liquor thereof by centrifuging. Subsequently, the solid matter is introduced into a drier 600 for drying, resulting in a powder of basic copper carbonate being provided.



A pH of the mixed solution in the reaction tank 9 below 8.0 causes a chlorine concentration of the thus-obtained basic copper carbonate to be increased, whereas the pH above 9.0 causes the basic copper carbonate to be partially changed into copper oxide and leads to an increase in the amount of alkali used. Thus, in the illustrated embodiment, the pH is preferably set within a range of between 8.0 and 9.0.

A reaction temperature of the mixed solution (temperature of the mixed solution) in the reaction tank 9 which is 70°C or below would permit a chlorine concentration of the basic copper carbonate to be reduced when the reaction time is increased. However, a reduction in chlorine concentration to a level below a reference level predetermined by the present invention is not attained even by the reaction extending over 8 hours, as will be noted from examples described below; thus, the reaction temperature at 70°C or below is not commercially accepted. On the contrary, the reaction temperature at 75°C leads to a satisfactory reduction in chlorine concentration by the reaction for, for example, 1.5 hours or more. The chlorine concentration tends to be decreased with an increase in reaction temperature when the reaction time is rendered the same. However, in the illustrated embodiment, the reaction temperature above 95°C causes an increase in chlorine concentration as will be noted from the examples described below. Also, even when the reaction temperature is set at a target value, it is unavoidable that the temperature is actually somewhat varied. Thus, in the illustrated embodiment, the reaction temperature, the target value is necessarily set to be within a range of between 75°C and 90°C.

The illustrated embodiment is directed to the method of the batch type. Alternatively, the method of the illustrated embodiment may be continuously practiced, for example, in a manner to discharge the mixed solution from an upper peripheral edge of the reaction tank while upwardly feeding an aqueous cupric chloride solution and an aqueous cupric sulfate solution to the reaction tank from a bottom thereof. In such continuous processing, the reaction time is defined to be a period of time for which the solution resides or is retained in the reaction tank.

The copper ion source which is a material for the basic copper carbonate may be constituted by an aqueous cupric sulfate solution in place of an aqueous cupric chloride solution. This causes  $\text{SO}_4$  to be introduced from the cupric sulfate into the basic copper carbonate. In this instance, reaction conditions for permitting a reduction in  $\text{SO}_4$  concentration which include a pH of the mixed solution, a reaction temperature thereof and a reaction time thereof are the same as those for reducing introduction of Cl from cupric chloride into the basic copper carbonate. A concentration of copper in the aqueous cupric chloride solution is preferably within a range of, for example, between 5% by weight and 24% by weight. A concentration



a pH (detected pH) of 8.0 when the temperature is reduced to a level of 75°C. Thus, it is supposed that even when the aqueous solution has an apparent pH(detected pH) of 8.0 at about 95°C, the actual pH is different from the apparent pH. This means that when the actual pH is 8.0, the apparent pH is out of 8.0. This would cause the feed ratio at 95°C to be considerably different from that at 75°C, resulting in the aqueous cupric chloride solution being excessively fed as compared with the aqueous sodium carbonate solution, leading to an increase in Cl concentration.

Thus, when the reaction temperature is set to be 95°C or more, the feed ratio rather than pH is controlled. A range in which the feed ratio is set is varied depending on a concentration of the mixed solution. Thus, in the present invention, a molar ratio between a copper ion and a carbonate ion in the mixed solution is defined for the feed ratio. Thus, when the aqueous cupric chloride solution is used, the aqueous cupric chloride solution and an aqueous solution containing a carbonate ion are fed to a reaction tank 9 while adjusting the feed ratio so as to ensure that a molar ratio between the copper ion and the carbonate ion in the mixed solution is 1:1.3 to 2.6. When the aqueous cupric sulfate solution is used, the aqueous cupric sulfate solution and the aqueous solution containing the carbonate ion are fed to the reaction tank 9 while adjusting the feed ratio so as to ensure that a molar ratio between the copper ion and the carbonate ion in the mixed solution is 1:2.3 to 4.6.

The method of the illustrated embodiment may be executed by means of a continuous processing apparatus shown in Fig. 6 by way of example. The continuous processing apparatus of Fig. 6 is constructed in such a manner that a reaction tank 9 has feed lines 100 and 200 connected to, for example, a bottom thereof and is configured so as to discharge the solution through an overflow portion 93 formed on an upper peripheral edge thereof. A control section 400 controls flow control sections 101 and 201 depending on a feed ratio (set value of feed ratio) between the aqueous cupric chloride solution and the aqueous sodium carbonate solution which permits a molar ratio between the copper ion and the carbonate ion to be 1:1.3 to 2.6, to thereby control the feed ratio. The aqueous solutions thus fed to the reaction tank 9 are held therein for a predetermined period of time, during which the solutions are reacted with each other. Then, the mixed solution is outwardly discharged through the overflow portion 93. In the illustrated embodiment, a pH detection section 301 may be arranged so as to monitor a pH of the mixed solution, to thereby output any alarm and provide a warning to an operator when a value detected is out of a predetermined range. Such construction ensures stabilization of the processing.

As can be seen from the foregoing, the illustrated embodiment not only permits a reduction in concentration of each of Cl and SO<sub>4</sub> contained in

the basic copper carbonate, but reduces alkaline metal such as sodium and/or alkaline earth metal incorporated from the carbonate into the plating bath. Accumulation of alkaline metal and/or alkaline earth metal in the plating bath causes sulfate thereof to be possibly deposited on a surface of an article plated. In order to avoid such a problem, it is required to increase the number of times of refreshment of the plating bath. The illustrated embodiment constructed as described above effectively eliminates the disadvantage.

The thus-obtained basic copper carbonate may be fed as a copper supply for copper plating to such an apparatus as described above with reference to Fig. 2.

The illustrated embodiment of the present invention will be understood more readily understood with reference to the following examples; however, these examples are intended to illustrate the invention and not to be construed to limit the scope of the invention.

#### Example 5-1

A laboratory-scale apparatus constructed in correspondence to the apparatus shown in Fig. 5 was used. A reaction tank of the apparatus was previously filled therein with a suitable amount of pure water, which was kept at a temperature of 75°C while being stirred. Then, the reaction tank was fed therein with the aqueous cupric chloride solution and aqueous sodium carbonate solution so as to render a pH target value (controlled pH) constant and was heated by a heater so as to maintain a reaction temperature therein constant. Then, the mixed solution was stirred to deposit or precipitate basic copper carbonate in the reaction tank, which was then subjected to solid-liquid separation, to thereby obtain a powder of basic copper carbonate. The reaction conditions were as follows:

Aqueous cupric chloride solution:

Copper concentration of 10% by weight

Aqueous sodium carbonate solution:

Carbonate ion concentration of 7% by weight

Reaction time in reaction tank: 2 hours

Reaction temperature: 75°C

pH target value: 8.0

The reaction temperature was slightly varied within a range of 75°C  $\pm$  2°C. Also, pH was likewise slightly varied within a range of 8.0  $\pm$  0.2. Then, a concentration of each of Cl and Na in the thus-obtained basic copper carbonate was measured. Results thereof were as shown in Table 5. Table 5 shows results of Example 5-2 to Comparative Example 5-3 as well.

Table 5

	Reaction Temp. (°C)	Reaction Time (Hr)	pH	Cl (ppm)	Na (ppm)
Ex.* 5-1	75	2	8.0	75	
Ex. 5-2	75	2	8.5	65	
Ex. 5-3	75	2	8.75	60	
Ex. 5-4	75	2	9.0	50	
Ex. 5-5	80	2	8.0	70	3200
Ex. 5-6	90	2	8.0	40	1800
Ex. 5-7	75	4	8.0	60	2200
Ex. 5-8	75	8	8.0	40	1500
Ex. 5-9	75	2	8.0	30	100
Ex. 5-10	75	2	8.0	60	1400
Ex. 5-11	75	4	8.5	40	1800
Ex. 5-12	75	1.5	8.0	80	
Com. Ex.** 5-1	75	2	7.3	150	
Com. Ex. 5-2	70	2	8.0	170	
Com. Ex. 5-3	70	8	8.0	100	

Ex.\*: Example

Com. Ex.\*\*: Comparative Example

Examples 5-2, 5-3 and 5-4

Basic copper carbonate was obtained by substantially repeating the procedure of Example 5-1 except that the pH target value was set to be 8.5, 8.75 and 9.0, respectively.

Examples 5-5 and 5-6

Basic copper carbonate was obtained by substantially repeating the procedure of Example 5-1 except that the reaction temperature was set to be 80°C and 90°C, respectively.

Examples 5-7 and 5-8

Basic copper carbonate was obtained by substantially repeating the procedure of Example 5-1 except that the reaction time was set to be 4 hours and 8 hours, respectively.

Examples 5-9 and 5-10

Basic copper carbonate was obtained by substantially repeating the procedure of Example 5-1 except that a carbonate ion concentration of the aqueous sodium carbonate solution was set to be 2.0% by weight and 3.5% by weight, respectively.

#### Example 5-11

Basic copper carbonate was obtained by substantially repeating the procedure of Example 5-1 except that the reaction time was set to be 4 hours and the pH target value was set to be 8.5.

#### Example 5-12

Basic copper carbonate was obtained by substantially repeating the procedure of Example 5-1 except that the reaction time was set to be 1.5 hours.

#### Comparative Example 5-1

Basic copper carbonate was obtained by substantially repeating the procedure of Example 5-1 except that the pH target value was set to be 7.3

#### Comparative Example 5-2

Basic copper carbonate was obtained by substantially repeating the procedure of Example 5-1 except that the reaction temperature was set to be 70°C, the pH target value was set to be 8.0, and the reaction time was set to be 2 hours.

#### Comparative Example 5-3

Basic copper carbonate was obtained by substantially repeating the procedure of Example 5-1 except that the reaction temperature was set to be 70°C, the pH target value was set to be 8.0 and the reaction time was set to be 8 hours.

The results shown in Table 5 clearly indicate that setting of the reaction temperature at 75°C or more and setting of pH at 8.0 or more permit a concentration of Cl contained in the basic copper carbonate to be reduced to a level of 80ppm or less aimed at by the present invention.

#### Example 6-1

Basic copper carbonate was obtained by substantially repeating the procedure of Example 5-1 except that an aqueous cupric sulfate solution having a copper concentration of 5% by weight was substituted for the aqueous cupric chloride solution.

#### Examples 6-2 and 6-3

Basic copper carbonate was obtained by substantially repeating the procedure of Example 6-1 except that the reaction temperature was set to be 80°C and 90°C, respectively.

#### Example 6-4

Basic copper carbonate was obtained by substantially repeating the procedure of Example 6-1 except that the reaction time was set to be 1.5 hours.

#### Comparative Example 6-1

Basic copper carbonate was obtained by substantially repeating the procedure of Example 6-1 except that the pH target value was set to be 7.3.

A concentration of each of  $\text{SO}_4$  and Na contained in the basic copper carbonate obtained in each of the examples and comparative examples was measured. Results of the measurement were as shown in Table 6.

Table 6

	Reaction Temp. (°C)	Reaction Time (Hr)	pH	$\text{SO}_4$ (ppm)	Na (ppm)
Ex. 6-1	75	2	8.0	190	
Ex. 6-2	80	2	8.0	180	1830
Ex. 6-3	90	2	8.0	130	1030
Ex. 6-4	75	1.5	8.0	200	
Com. Ex. 6-1	75	2	7.3	510	

In Example 6-1 to Comparative Example 6-1, substitution of the aqueous cupric sulfate solution for the aqueous cupric chloride solution causes an anion introduced into the basic copper carbonate to be  $\text{SO}_4$  rather than Cl. Thus, it will be readily expected that employment of the same reaction conditions as in the aqueous copper chloride solution leads to a reduction in concentration of  $\text{SO}_4$ . For the sake of confirmation, a variation in  $\text{SO}_4$  concentration depending on a variation in pH was measured. As a result, the concentration was increased to a level as high as 510ppm when pH is below 8.0; whereas it was reduced to a level as low as 200ppm or less when pH is at 8.0.

#### Example 7-1

Basic copper carbonate was obtained by substantially repeating the procedure of Example 5-1 except that the reaction temperature was set to be each of 75°C, 80°C, 90°C, 95°C and 100°C. Then, a concentration of Cl in each of the basic copper carbonates thus obtained was measured. Results of the measurement were as shown in Table 7. (Results in connection with 75°C, 80°C and 90°C were described above.) Also, a feed ratio of the aqueous sodium carbonate which constitutes an alkali side to the aqueous cupric chloride solution which constitutes an acid side (fed amount of an

aqueous sodium carbonate solution divided by fed amount of an aqueous cupric chloride solution) was as shown in Table 7.

Table 7

	Reaction Temperature (°C)				
	75	80	90	95	100
Cl Concentration (ppm)	75	70	40	110	50000
Feed Ratio	2.0	1.9	1.8	1.5	1.2

The results of Table 7 indicate that when the reaction temperature is 95°C or more, control of the feed ratio by pH control causes the aqueous cupric chloride solution which is a Cl source to be relatively excessively fed for the same reason, resulting in the Cl concentration of the basic copper carbonate being increased.

In view of the above, a reaction was carried out which permits a feed ratio at a temperature of 95°C to be 1.8 which is a feed ratio obtained at a temperature of 90°C and a pH of 8.0. Also, a reaction which permits a feed ratio at a temperature of 100°C to be 2.0 which is a feed ratio obtained at a temperature of 75°C and a pH of 8.0 was carried out. As a result, the basic copper carbonates obtained by the reactions had a Cl concentration of 35ppm and 40ppm, respectively. Thus, it will be noted that when the reaction temperature is set to be 95°C or more, it is effective to carry out control so as to render the feed ratio constant or set it within a predetermined range without carrying out pH control.

#### Example 7-2

Basic copper carbonate was obtained by substantially repeating the procedure of Example 6-1 except that the aqueous cupric sulfate solution was substituted for the aqueous cupric chloride and the reaction temperature was set to be each of 75°C, 80°C, 90°C, 95°C and 100°C. Then, a concentration of SO<sub>4</sub> in each of the basic copper carbonates thus obtained was measured. Results of the measurement were as shown in Table 8. (Results in connection with 75°C, 80°C and 90°C were described above.) Also, a feed ratio of the aqueous sodium carbonate which constitutes an alkali side to the aqueous cupric sulfate solution which constitutes an acid side was as shown in Table 8.

Table 8

	Reaction Temperature (°C)				
	75	80	90	95	100
SO <sub>4</sub> Concentration (ppm)	190	180	130	360	15000
Feed Ratio	1.8	1.7	1.6	1.3	1.0



The results of Table 8 indicate that the reaction temperature of 95°C or more causes an increase in difference between the actual pH and the apparent pH as described above with respect to the embodiment shown in Fig. 6, so that control of the feed ratio by pH control causes the aqueous cupric sulfate solution acting as a SO<sub>4</sub> source to be relatively excessively fed, resulting in the SO<sub>4</sub> concentration of the basic copper carbonate being increased.

In view of the above, a reaction was carried out which permits a feed ratio at a temperature of 95°C to be 1.6 which is a feed ratio obtained at a temperature of 90°C and a pH of 8.0. Also, a reaction which permits a feed ratio at a temperature of 100°C to be 1.8 which is a feed ratio obtained at a temperature of 75°C and a pH of 8.0 was carried out. As a result, the basic copper carbonates obtained by the reactions had a SO<sub>4</sub> concentration of 200ppm and 120ppm, respectively.

#### Example 8-1

Copper electroplating was executed using basic copper carbonate having a Cl concentration(chloride concentration) of about 50ppm as a copper supply under the following conditions:

##### Electroplating Conditions:

Anode: Titanium plate coated with platinum alloy

(Pt:Ir=7:3)

Cathode: Copper plate

Electrode area: 10cm x 10cm

Current density, current, voltage: 1 A/dm<sup>2</sup>, 1A, 2.2V

Copper concentration: 18 g/l in terms of Cu

Concentration of sulfuric acid: 180 g/l in terms of H<sub>2</sub>SO<sub>4</sub>

A chlorine concentration in the plating bath at the time of starting of the plating was adjusted to be about 20ppm. When basic copper carbonate was fed so as to keep the copper concentration constant, a chlorine concentration in the plating bath was increased to a level of 1 to 2 ppm/day. However, the Cl concentration was rendered constant at the time when the Cl concentration in the plating bath reached a level of about 40ppm. An increase in Cl concentration was not observed even after lapse of 40 days. Thus, it would be considered that the amount of chlorine generated from the anode is balanced with the amount of chlorine contained in basic copper carbonate oxide fed. The cathode ultimately obtained had a highly flat and smooth surface.

#### Example 8-2

Copper electroplating was executed by substantially repeating the

procedure of Example 8-1 except that basic copper carbonate having a  $\text{SO}_4$  concentration of about 150ppm was used as a copper supply.

The copper electroplating was started while keeping an initial sulfuric acid concentration in the plating bath at 180 g/l. When basic copper carbonate was fed so as to keep the copper concentration constant, a  $\text{SO}_4$  concentration in the plating bath was increased to a level of 9 mg/day. Volatilization of  $\text{SO}_4$  from the plating bath or the like was not observed. Accumulation of  $\text{SO}_4$  in the plating bath was very slow, therefore, it would be considered that dilution of the plating bath or the like is not required for control of the  $\text{SO}_4$  concentration in the plating bath.

#### Comparative Example 8-1

Copper electroplating was executed by substantially repeating the procedure of Example 8-1 except that basic copper carbonate having a Cl concentration of about 200ppm was used as a copper supply.

A chlorine concentration in the plating bath at the time of starting of the plating was adjusted to be about 20ppm. When basic copper carbonate was fed to the plating bath so as to keep the copper concentration constant, a Cl concentration in the plating bath was increased to a level of 3 to 4 ppm/day. This would be due to the fact that the amount of chlorine generated from the anode is reduced as compared with the amount of chlorine contained in basic copper carbonate oxide fed. After lapse of 40 days, the Cl concentration in the plating bath was increased to about 160ppm. The cathode ultimately obtained had a coarse surface as compared with that obtained in Example 8-1.

#### Comparative Example 8-2

Copper electroplating was executed by substantially repeating the procedure of Example 8-2 described above except that basic copper carbonate having a  $\text{SO}_4$  concentration of about 500ppm was used as a copper supply.

The copper electroplating was started while keeping an initial sulfuric acid concentration in the plating bath at 180 g/l. When basic copper carbonate was fed to the plating bath so as to keep the copper concentration constant, a  $\text{SO}_4$  concentration in the plating bath was increased to a level of 30 mg/day. Volatilization of  $\text{SO}_4$  from the plating bath or the like was not observed. This caused  $\text{SO}_4$  to be accumulated in the plating bath, so that it was required to carry out dilution or the like in order to control of the  $\text{SO}_4$  concentration in the plating bath.

In view of the results of Example 8-1 to Comparative Example 8-2, it is expected that when a Cl concentration of the basic copper carbonate is 80 ppm or less, no increase of the Cl concentration in the plating bath is observed, resulting in satisfactory copper electroplating. Thus, a Cl concentration of the basic copper carbonate is preferably 80 ppm or less.

It is also expected that when a  $\text{SO}_4$  concentration of the basic copper carbonate is 200 ppm or less, accumulation of  $\text{SO}_4$  is delayed. It is further expected to take a long period until dilution or the like is required to control of the  $\text{SO}_4$  concentration in the plating bath, even if necessary. Thus,  $\text{SO}_4$  concentration of the basic copper carbonate is preferably 200 ppm or less.

As can be seen from the foregoing, the present invention provides a copper electroplating material which is easily dissolved, minimizes formation of an insoluble residue and ensures satisfactory copper plating. Also, copper electroplating by means of the copper electroplating material of the present invention minimizes the number of times of refreshment of the plating bath, to thereby restrain an increase in plating cost.

While preferred embodiment of the invention have been described with a certain degree of particularity with reference to the drawings, obvious modifications and variations are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

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